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Regeneration of a hydrogenation catalyst

The invention relates to a process for regenerating a hydrogenation catalyst.

Hydrogenation catalysts are used in many chemical reactions. They generally comprise elements of group VIII of the Periodic Table, e.g. iron, cobalt, nickel, ruthenium, rhodium, palladium, platinum and iridium, as active components. Promoters such as copper, silver, gold, zinc, tin, bismuth or antimony may additionally be present.

Hydrogenation catalysts are frequently used in supported form, with the active component being applied to a support. Support materials used are frequently metals, oxidic materials such as aluminum oxide or silicon dioxide, carbon fibers or polymers.

As a result of secondary reactions, oligomers and polymers, known as green oil, are formed from the reactants in the hydrogenation reactors, and these lead to carbon-containing deposits on the hydrogenation catalyst. As a result, pores become blocked, active centers become inaccessible, the activity of the catalyst decreases and regeneration of the catalyst becomes necessary. In the classical regeneration method, the carbon-containing deposits are burnt oxidatively, frequently by passing air over the catalyst at elevated temperatures of from about 400 to 500°C. To avoid local overheating, water vapor is frequently added. A disadvantage of this classical regeneration is that the activity of the regenerated catalyst is generally lower than that of the fresh catalyst.

It is known from WO 94/00232 that a catalyst which has previously been used for removing acetylenic impurities from an olefin stream can be regenerated virtually completely by stripping with a stream of hydrogen at a linear velocity of at least 15.2 cm/second at from 315 to 400°C, without oxidative treatment.

WO 02/00341 describes a regeneration process for hydrogenation catalysts which comprises passing a hydrogen-containing gas stream over the catalyst at from 200 to 1000°C, without combustion using an oxygen-containing gas.

GB-B 907,348 discloses a process for regenerating a nickel catalyst applied to an inert support which has been used in the selective hydrogenation of petroleum spirit, in which

the catalyst is treated in-situ or ex-situ with a hydrogen-containing gas at 150°C for from 1 to 24 hours.

It is an object of the present invention to provide a process for regenerating a hydrogenation catalyst which has been used in a gas-phase hydrogenation, by means of which the original activity of the fresh hydrogenation catalyst is largely restored.

We have found that this object is achieved by a process for regenerating a hydrogenation catalyst which has been used in a gas-phase hydrogenation, which comprises stripping at from 50 to 300°C with a substance or a substance mixture which under the process conditions has no oxidizing action and is present in the gaseous state.

In the stripping process of the present invention, a substance or a substance mixture which is gaseous at the process temperature in the range from 50 to 300°C is therefore passed over the used hydrogenation catalyst. In this process, the relatively volatile components of the green oil are carried out in gaseous form, while less volatile components of the green oil which had coated and thus deactivated the hydrogenation catalyst during operation are melted and flow away.

It is important for the purposes of the present invention that a stripping gas which has no oxidizing action under the process conditions is chosen.

It has surprisingly been found that the original activity of the fresh catalyst can be restored virtually completely by regeneration by means of the process of the present invention, even though the surface of the hydrogenation catalyst was largely coated with carbon after the purification process.

The process of the present invention can advantageously be used to regenerate a hydrogenation catalyst which has previously been used in the selective hydrogenation of a C_2 and/or C_3 fraction. This hydrogenation can be either a front-end hydrogenation or a tail-end hydrogenation. Such a process and a catalyst particularly suitable for this purpose are known from DE-A 19959064, whose disclosure is hereby fully incorporated by reference into the present patent application.

As stripping gas, it is in principle possible to use any substance or any substance mixture which does not have an oxidizing action on the hydrogenation catalyst. The substance or substance mixture is preferably selected from the group consisting of hydrogen, nitrogen, argon, hydrocarbons, preferably saturated hydrocarbons, particularly preferably methane.

Nitrogen is particularly advantageous, especially because of its availability, its price and its heat capacity; a mixture of nitrogen and hydrogen is similarly advantageous.

Stripping is advantageously carried out at from 70 to 150°C, in particular from 100 to 150°C.

The stripping time is preferably from 30 minutes to a number of days, particularly preferably from one hour to 2 days. At a higher temperature, a shorter process time is preferred.

In a further process variant, the hydrogenation catalyst is rinsed with a preferably nonpolar organic solvent or solvent mixture in addition to stripping. Any solvent or solvent mixture which at least partly dissolves the carbon-containing deposits on the hydrogenation catalyst is suitable for this purpose. Hydrocarbons, for example cyclohexane or a benzene/toluene/xylene fraction, are particularly useful.

Rinsing is preferably carried out at from 20 to 50°C, particularly preferably at ambient temperature. The upper limit for the process temperature depends on the boiling point of the solvent or solvent mixture used, i.e. it should be no higher than this boiling point. A process time of from 50 minutes to a number of days is generally sufficient for rinsing.

The hydrogenation of the hydrogenation catalyst can be carried out in situ, in supernatant solvent and/or in solvent circulated by means of a pump. However, it is also possible to remove the hydrogenation catalyst from the reactor, i.e. rinse it ex-situ, preferably in supernatant solvent and/or in circulating solvent, preferably with additional introduction of gas and/or with the aid of ultrasound.

Particular preference is given to carrying out the hydrogenation by firstly rinsing the hydrogenation catalyst and subsequently stripping it.

If the hydrogenation catalyst is regenerated for more than the first time, it can be advantageous, after the catalyst has been treated two or more times by stripping or rinsing and stripping as described above, to regenerate it by oxidative treatment or by a combination of stripping or rinsing and stripping and oxidative treatments. This will be necessary when coating with carbon-containing deposits has progressed a long way.

The process is particularly useful for regenerating hydrogenation catalysts in the form of thin-film catalysts. Thin-film catalysts have a thickness of the active material in the range

from about 0.01 μm to 100 μm. Thin-film hydrogenation catalysts are described, for example, in EP-A 0 412 415, EP-A 0 564 830 or EP-A 0 965 384 and are obtained by impregnation (EP-A 0 412 415), vapor deposition under reduced pressure (EP-A 0 564 830) or sputtering (EP-A 0 965 384).

The thin-film hydrogenation catalyst is preferably made up of an active composition comprising one or more hydrogenation-active metals, in particular palladium, particularly preferably silver-doped palladium, which has been applied to a nonporous, preferably metallic support which is preferably in the form of a woven mesh or knitted mesh.

The invention is illustrated below by means of examples.

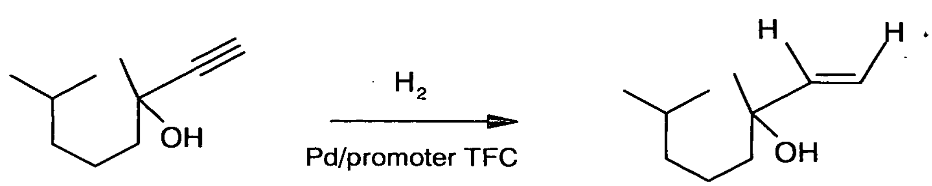
The catalysts tested were monolithic thin-film hydrogenation catalysts, hereinafter referred to as TFCs for short, which comprised palladium as active composition and silver as promoter on a knitted stainless steel mesh support and had been obtained as follows:

A 20 cm wide strip of knitted metal mesh made of the material No. 1.4301 and having a wire diameter of 0.12 mm was heated in a muffle furnace. After cooling to room temperature, the knitted mesh which had been pretreated in this way was rolled up.

It was subsequently treated with an impregnation solution comprising palladium nitrate, silver nitrate and distilled water.

The impregnated knitted metal mesh was dried and calcined in air.

The TFC produced in this way was used in a process for the selective hydrogenation of hydro-dehydro-linalool (HDHL) to hydro-linalool (H-LIN), which proceeds according to the following reaction equation:



Hydro-dehydro-linalool

Hydro-linalool

The reaction was carried out continuously and isothermally in the upflow mode in a packed bubble column in a laboratory glass apparatus. The catalyst consisted of 2 monoliths made

from the above-described knitted metal mesh, in each case having a height of 200 mm and a length of 300 mm and wound to a final diameter of 22 mm. The substrate volume was 0.5 kg of HDHL having a purity of 99%.

The following process parameters were set:

Pressure:	1.1 bar
Temperature:	80°C
Circulation of reaction liquid:	200 $m^3/m^2/h$
Gas circulation (hydrogen):	200 $m^3/m^2/h$

Examples 1 to 7 and comparative examples C1 to C3:

Influence of regeneration temperature and time on the catalyst activity

A TFC as described above was tested under the above-described process conditions. The TFC was converted by reduction with hydrogen into a hydrogenation active form and subsequently, to simulate deactivation, steeped in green oil. For comparison, the TFC was regenerated by the classical, oxidative treatment with steam/air or, according to the present invention, by means of nitrogen. Regeneration temperature and time were varied and the catalyst activity after regeneration was measured by means of the relative conversion in the above-described selective hydrogenation of HDHL, with the conversion over fresh catalyst being assigned a value of 100%.

The experimental results are summarized in Table 1 below:

	Treatment	Temperature [°C]	Time	Rel. conversion %
C1	Steam/air	400	4h	79
C2	Steam/air	400	24h	63
1	N_2	100	4h	98
2	N_2	150	4h	89
3	N_2	200	4h	81
C3	N_2	400	4h	52
4	N_2	100	4h	98
5	N_2	100	24h	84
6	N_2	150	24h	83

The results show that increasing the temperature and time of the regeneration has adverse effects on the catalyst activity after the regeneration.

Comparative examples C4 and C5 and examples 7 and 8:

Influence of the regeneration method on the activity of a TFC which has been used in a production reactor for the selective hydrogenation of a C_3 fraction

The TFC obtained by the above-described method and shaped to form packets as described in DE-A 100 05 663 was used in a production reactor for the selective hydrogenation of propyne and/or propadiene in C_3 fractions to propylene, referred to as "Process B" in DE-A 19959064. After a running time of one year, the catalyst was removed from the reactor and characterized as such, i.e. without regeneration (comparative example C4), after classical, oxidative regeneration using a steam/air mixture at 400°C (comparative example C5), after regeneration according to the present invention by stripping with a stream of nitrogen at 100°C for 24 hours (example 8) and after regeneration according to the present invention by means of brief stripping with nitrogen in the reactor and subsequent rinsing with a benzene/toluene/xylene solvent mixture under the following process conditions:

Solvent mixture volume/catalyst volume: 1.5:1
Time: 6 hours
Temperature: 25°C
(example 9 according to the present invention).

In all comparative examples (C4, C5) and examples (7, 8), the following properties of the TFC were determined:

Diameter of the primary particles in nanometers by means of transmission electron microscopy,
Carbon content at the surface of the TFC in atom percent (atom-%), measured by means of X-ray photoelectron spectroscopy and
Relative conversion C(rel.) for the selective hydrogenation of HDHL to H-LIN, based on 100% conversion for the fresh TFC.

The results are summarized in table 2 below:

	Regeneration method	Diameter [nm]	C content [atom-%]	C(rel.) [%]
C4	-	10 - 20	94	85
7	N_2 stripping	10 - 20	85	94
C5	Classical	100	19	65
8	Stripping, rinsing	10 - 20	78	94

The experimental results show that the diameter of the primary particles is not changed by the regeneration methods of the present invention. Although the carbon content at the catalyst surface decreases, albeit only insignificantly, compared to the classical oxidative regeneration method, this is surprisingly not a decisive factor in determining the catalyst activity, i.e. the achievable conversions. In contrast, the regeneration method of the present invention achieves conversions which are only slightly below the conversions obtained using the fresh catalyst.